(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 January 2005 (27.01.2005)

PCT

(10) International Publication Number
WO 2005/007939 A1

(51) International Patent Classification[7]: C30B 11/00, 29/40, 29/42

(21) International Application Number: PCT/JP2004/010555

(22) International Filing Date: 16 July 2004 (16.07.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003-275987 17 July 2003 (17.07.2003) JP
60/489,494 24 July 2003 (24.07.2003) US

(71) Applicant *(for all designated States except US)*: **SHOWA DENKO K.K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **MATSUMOTO, Fumio** [JP/JP]; c/o SHOWA DENKO K.K., 1505, Shimokagemori, Chichibu-shi, Saitama 369-1871 (JP).

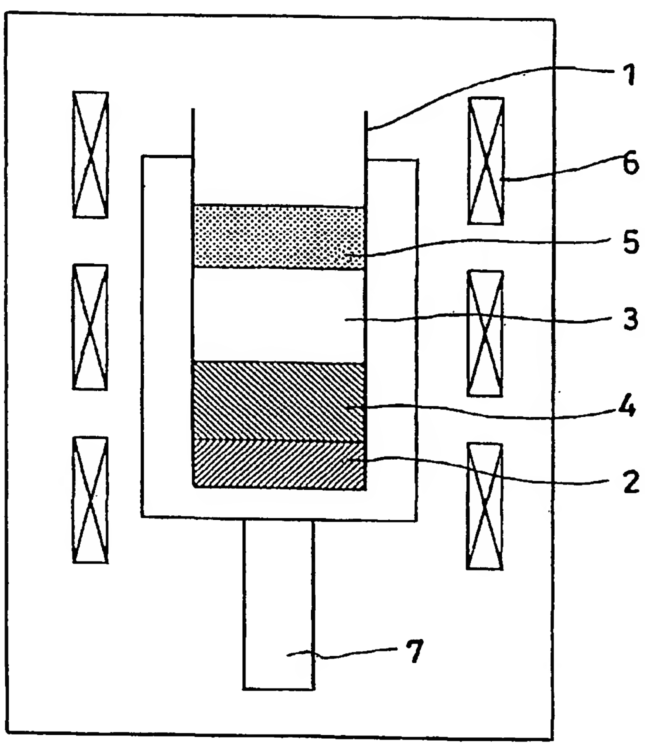
(74) Agents: **FUKUDA, Kenzo** et al.; Kashiwaya Building, 6-13, Nishishinbashi 1-chome, Minato-ku, Tokyo 105-0003 (JP).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

[Continued on next page]

(54) Title: InP SINGLE CRYSTAL, GaAs SINGLE CRYSTAL, AND METHOD FOR PRODUCTION THEREOF



(57) Abstract: A method for the production of an InP single crystal includes gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and grow a single crystal, causing the seed crystal to possess an average dislocation density of less than $10000/cm^2$ and assume substantially identical cross-sectional shape and size with a crosssectional shape and size of a single crystal to be grown, and allowing the InP single crystal to be grown to retain a non-doped state or a state doped with Fe or Sn.

WO 2005/007939 A1

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION

InP SINGLE CRYSTAL, GaAs SINGLE CRYSTAL, AND METHOD FOR PRODUCTION THEREOF

Cross Reference to related Applications:

This application is an application filed under 35 U.S.C. § 111(a) claiming the benefit pursuant to 35 U.S.C. § 119(e)(1) of the filing date of Provisional Application No. 60/489,494 filed July 24, 2003 pursuant to 35 U.S.C. § 111(b).

Technical Field:

This invention relates to a method for the production of an indium phosphide (InP) and a gallium arsenide (GaAs) compound semiconductor single crystals of low dislocation density by the vertical gradient freezing technique (hereinafter referred to as "VGF technique") or the vertical Bridgman technique (hereinafter referred to as "VB technique").

Background Art:

As a method for the production of a GaAs single crystal and an InP single crystal, the liquid encapsulated Czochralski process (hereinafter referred to as "LEC process") has been generally utilized heretofore. While the LEC process enjoys a strong point of enabling a wafer of a large diameter to be manufactured comparatively easily, it entails a defect of forming a large temperature gradient in the axial direction during the growth of crystal and consequently suffering from a high dislocation density that affects the characteristics and the life of a component.

In contrast, the VGF technique and the VB technique enjoy a strong point of allowing the dislocation density to be easily decreased because they are capable of setting small temperature gradients in the axial direction. Since they execute the growth of crystal in a low temperature gradient, they suffer from a weak point of encountering difficulty in obtaining a single crystal of a low dislocation density with high reproducibility because they tend to induce generation of a twin crystal due to uneven growth caused by a fluctuation of the temperature within the furnace, dislocation

propagated from a seed crystal within the crystal in growth, and polycrystallization due to the accumulation of dislocations generated by thermal stress after the growth.

Particularly in the case of the growth of an InP crystal by the VGF technique or the VB technique, since the stacking fault energy thereof which bears on the generation of a twin crystal is smaller than that of the GaAs crystal, this growth of the crystal entails the problem of easily generating a twin crystal and extremely degrading the yield of a single crystal. Regarding this matter, the success attained by the use of a seed crystal substantially identical in cross-sectional shape and size with a target crystal in obviating the necessity for making a complicate control of crystal growth relative to a diameter-increased part, simplifying the structure of a crucible, diminishing the loss of crystal liable to occur in the diameter-increased part, realizing a decrease of the dislocation density and enabling a single crystal to be obtained in high yield has been reported (for example, in (JP-A HEI 3-40987), (Advanced Electronics Series 1-4, "Technology of Bulk Crystal Growth," compiled and written by Keigo Hoshikawa, published by Baifukan, p. 239) and (U. Sahr, et. al: 2001 International Conference on Indium Phosphide and Related Materials: "Growth of S-doped 2" InP-Crystals by the Vertical Gradient Freeze Technique, pp 533-536)).

When a crystal grown by the ordinary LEC process is used as a non-doped seed crystal having a dislocation density on the order of $70000/cm^2$, the growth of this non-doped crystal enables the crystal of the grown part to acquire an average dislocation density of $7000/cm^2$, i.e. a decrease to the order of 1/10 or less of the original level, and nevertheless entails the problem that this decrease fails to reach the target level of $5000/cm^2$ or less.

Consequently, the Fe-doped InP crystals intended for high-speed electronic devices that are used in popular high-frequency devices and the Sn-doped InP crystals intended mainly for light-receiving devices have dislocation densities of similar degrees. It is difficult for them to lower their average dislocation densities to below the target level of $5000/cm^2$ or less.

As regards the S-doped InP crystals, Zn-doped InP crystals and the Si-doped or Zn-doped GaAs crystals which are used in the laser devices, the wafers formed of these crystals are required to possess extremely low dislocation densities because the

dislocations in the wafers have a great effect to bear on the lives of the laser devices.

These wafers are required to have a low dislocation density of less than 500/cm^2 in most of the regions thereof. When the non-doped crystal grown by the ordinary LEC process is used as a seed crystal, the average dislocation density can be lowered to about 1000/cm^2 owing to the hardening action of such impurities of S element, Zn element or Si element incorporated as a dopant. It is, however, difficult for this crystal to lower the average dislocation density thereof to the target level of less than 500/cm^2 throughout the entire region of a wafer.

In the production of the GaAs single crystal, the VGF technique or VG technique that obtains the single crystal of a diameter aimed at by forming an increased-diameter part while pulling a thin seed crystal is generally employed. This technique indeed obtains the single crystal having an average dislocation density aimed at but entails the problem of producing the single crystal only in a low yield. This low yield of the growth of this single crystal is ascribed to the fact that since the use of the slender seed crystal requires the seed crystal to grow via the increased diameter part to the straight barrel part while varying the diameter thereof accordingly, even a slight fluctuation of the temperature inside the furnace brings an influence of exalting the probability of generation of a twin crystal and generation of a polycrystal.

This invention has been initiated with a view to solving the problem mentioned above. It is aimed at providing a method which is capable of producing a single crystal of a high grade of average dislocation density with the object of affording InP single crystals intended for high-speed electronic devices for use in high-frequency devices, InP single crystals intended for light-receiving devices, or InP single crystals or GaAs single crystals intended for laser devices and providing a single crystal possessing an average dislocation density aimed at.

Disclosure of the Invention:

This invention provides a method for the production of an InP single crystal comprising gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and consequently grow a single crystal, causing the seed crystal to possess an

average dislocation density of less than 10000/cm^2 and assume substantially identical cross-sectional shape and size with a cross-sectional shape and size of a single crystal to be grown and allowing the InP single crystal to be grown to retain a non-doped state or a state doped with Fe or Sn.

In the method, the seed crystal embraces a seed crystal that possesses a largest dislocation density of less than 30000/cm^2.

In the method, the seed crystal embraces a seed crystal that has been manufactured from an InP single crystal produced by the method.

This invention also provides a non-doped, Fe-doped or Sn-doped InP single crystal possessing a dislocation density of less than 5000/cm^2 and produced by the aforementioned method.

This invention further provides a production method for the production of an InP single crystal comprising gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and consequently grow a single crystal, causing the seed crystal to possess an average dislocation density of less than 500/cm^2 and assume substantially identical cross-sectional shape and size with a cross-sectional shape and size of a single crystal to be grown and allowing the InP single crystal to be grown to retain a state doped with S or Zn.

In the production method, the seed crystal embraces a seed crystal that possesses a largest dislocation density of less than 3000/cm^2.

In the production method, the seed crystal embraces a seed crystal that has been manufactured from an InP single crystal produced by the production method.

This invention further provides an S-doped or Zn-doped InP single crystal that possesses a dislocation density of less than 500/cm^2 and is produced by the production method.

This invention also provides a method for the production of a GaAs single crystal comprising gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and consequently grow a single crystal, causing the seed crystal to possess an average dislocation density of less than 500/cm^2 and assume substantially identical cross-

sectional shape and size with a cross-sectional shape and size of a single crystal to be grown and allowing the GaAs single crystal to be grown to retain a state doped with Si or Zn.

In the method just mentioned above, the seed crystal embraces a seed crystal that possesses a largest dislocation density of less than 3000/cm^2.

In the method, the seed crystal embraces a seed crystal that has been manufactured from a GaAs single crystal produced by the method.

This invention further provides a Si-doped or Zn-doped GaAs single crystal possessing a dislocation density of less than 500/cm^2 and produced by the method.

This invention, in the growth of an InP single crystal as described above, results in growing a single crystal having an average dislocation density of 2000/cm^2 using a seed crystal having an average dislocation density of less than 10000/cm^2 or results in growing a single crystal having an average dislocation density of 500/cm^2 using a seed crystal having an average dislocation density of less than 500/cm^2.

The method of this invention can produce a single crystal of a high grade of average dislocation density aimed at as described above. The single crystals that are produced by the method of this invention, therefore, are used in high-speed electronic devices of high-frequency devices, light-receiving devices and laser devices.

Brief Description of the Drawing:

Fig. 1 is a schematic cross section of a crystal growth furnace that is used when this invention is applied to the VGF technique.

Fig. 2 is a schematic cross section of a seed crystal and a crucible used in an experiment of Comparative Example 3.

Best Mode for carrying out the Invention

This invention concerns a method for producing a single crystal by gradually cooling a molten raw material held in contact with a seed crystal, thereby solidifying the molten raw material successively from the lower part toward the higher part of the interior of a crucible and attaining growth of the single crystal and requires the seed crystal to be used to assume substantially identical cross-sectional shape and size with the

cross-sectional shape and size of a single crystal to be grown and possess an average dislocation density of less than 10000/cm^2 and preferably possess the largest dislocation density of less than 30000/cm^2.

As a result, a single crystal having the average dislocation density decreased to 1000/cm^2, i.e. a level about 1/10 of the original level, is grown.

For the sake of growing a single crystal having an extremely low dislocation density, it is proper to use a seed crystal that has an average dislocation density of less than 500/cm^2 and the largest dislocation density of less than 3000/cm^2.

By using a seed crystal of this grade which is not doped or which is doped with the same dopant as used in the crystal to be grown, a S-doped or Zn-doped InP single crystal or a Si-doped or Zn-doped GaAs single crystal is grown.

As a result, a single crystal having an average dislocation density of 500/cm^2 and befitting a laser device is grown so as to allow production of compound semiconductors of high quality inducing no twin crystal in a high yield.

Now, the embodiment of executing the growth of an InP crystal according to this invention will be described below.

Fig. 1 is a schematic cross section of a crystal growth furnace to be used in the application of this invention to the VGF technique. With reference to Fig. 1, a seed crystal 2 assuming substantially identical cross-sectional shape and size with the cross-sectional shape and size of a crystal to be grown and possessing a low dislocation density is set in place on the bottom part of a crucible made of PBN. A solid grown crystal 4 overlies the seed crystal 2, and a molten raw material 3 not yet crystallized overlies the crystal 4. The upper side of the molten raw material 3 is covered with a liquid sealant 5 (B_2O_3) for preventing vaporization of phosphorus from the molten raw material. The crucible 1 is provided on the peripheral surface thereof with a heater 6 which is adapted to keep the molten raw material 3 and the sealant 5 intact and form a temperature distribution such that the temperature will be retained on the seed crystal 2 side of the interior of the furnace at a low level for allowing the crystal to grow and will be heightened toward the upper part of the interior. A susceptor 7 serves the purpose of supporting the crucible.

These growth jigs are disposed inside a high-pressure vessel and the furnace has the interior thereof filled with an atmosphere of inert gas. The growth of a crystal is made by lowering the controlling temperature of the heater to thereby solidify the molten raw material from the seed crystal side upwardly. In the VB technique, the solidification is accomplished by relatively moving the heater and the crucible.

The seed crystal to be used properly possesses an average dislocation density of less than 10000/cm^2 and preferably the largest dislocation density of less than 30000/cm^2 as well. By using this seed crystal, a non-doped, Fe-doped or Sn-doped InP single crystal is grown. The seed crystal to be used for growing a crystal of an extremely low dislocation density properly possesses an average dislocation density of less than 500/cm^2 or the largest dislocation density of less than 3000/cm^2. By using a seed crystal having this grade of quality, a S-doped or Zn-doped InP single crystal or a Si-doped or Zn-doped GaAs single crystal is grown.

In the manufacture of a seed crystal having such a low dislocation density, the crystal that is manufactured by the ordinary LEC process cannot be easily used as the seed crystal because it imparts no sufficient decrease of dislocation density to the crystal to be grown. The present invention uses as the seed crystal the crystal of a low dislocation density that is grown by the modified LEC process capable of attaining the growth in a low temperature gradient under a controlled atmosphere of a Group V element or by the horizontal boat technique instead of the LEC process. It goes without saying that the crystal of a low dislocation density which has been grown by the VGF or VG technique according to the method of this invention can be used as the raw material for a seed crystal.

The method for determining the average dislocation density in a given crystal consists in measuring average dislocation densities at intervals of 5 mm in the radial direction within the surface of a given wafer and averaging the numerical values consequently obtained. The largest dislocation density of this crystal is determined by dividing the entire surface of the wafer into squares of 5 mm, measuring a dislocation density at one point in each of the squares of 5 mm, preparing an in-plane distribution of dislocation densities and finding the largest of numerical values shown in the in-plane distribution.

As the seed crystal, the non-doped crystal that has incorporated no element of any sort as a dopant therein can be generally used. The crystal that has been doped with the element that is same as the crystal to be grown can be also used. It is permissible to utilize the seed crystal repeatedly.

Now, concrete Examples of this invention will be described below. This invention does not need to be limited to the following Examples.

Example 1:

As a device for growing a crystal, a VGF furnace illustrated in Fig. 1 was used.

First, a crucible made of PBN and measuring 52 mm in inside diameter was charged with a seed crystal measuring 51.5 mm in diameter and 20 mm in thickness, 1000 g of an InP polycrystal raw material and 200 g of B_2O_3 and accommodated in a susceptor. The seed crystal was not grown by the ordinary LEC process but was grown by the modified LEC process using an atmosphere of phosphorus. This seed crystal possessed an average dislocation density of 8200/cm^2 and a largest dislocation density of 27000/cm^2. The susceptor vessel packed with the seed crystal, polycrystal raw material and B_2O_5 was disposed in the furnace. The furnace was then made to introduce argon gas as an inert gas till the interior pressure thereof reached 40 atmospheres (4 MPa). The heater was operated to heat the interior of the furnace to a temperature of about 1070°C so as to melt the B_2O_5 and the polycrystal raw material. After the thorough melting of the polycrystal raw material was confirmed, the temperature of the seed crystal part was made to equal the melting point of InP (1062°C) and the heater temperature was lowered in order for the crystal growth speed to reach 2 mm/hr. The crystal was grown for about 50 hours and the hot crystal was cooled to room temperature over a period of 10 hours.

After the grown crystal was cooled to room temperature, the furnace was opened to extract the crucible. The B_2O_3 in the PBN crucible was dissolved in alcohol so as to induce removal of the non-doped InP crystal. The crystal consequently obtained was an InP single crystal measuring 2 inches in diameter and 90 mm in total length and generating absolutely no twin crystal. When the single crystal ingot was cut and examined to determine dislocation density, it was found to be a single crystal having such a low average dislocation density of 1240/cm^2.

When five experiments were carried out on the growth of a non-doped InP single crystal by using a seed crystal having an average dislocation density of less than 10000/cm^2, the five experiments invariably avoided forming a twin crystal and obtained single crystals having lower dislocation densities than 2000/cm^2. Thus, they demonstrated successful production of an InP single crystal of low dislocation density with high reproducibility.

When a non-doped InP single crystal was grown by using as a new seed crystal the aforementioned grown part possessing an average dislocation density of 1240/cm^2, the single crystal ingot consequently obtained possessed a further lowered average dislocation density than in the previous growth of crystal, and the single crystal obtained from the ingot possessed an average dislocation density of 480/cm^2. The experiment has demonstrated that the use of a crystal having a low dislocation density as a seed crystal permits the growth of a single crystal possessing a further lower dislocation density.

While Example 1 has demonstrated the growth of a non-doped InP crystal, the growth of a Fe-doped InP crystal that is used in high-frequency electronic devices and the growth of an Sn-doped crystal that is used as the substrate for a light-receiving device can be accomplished in the same manner as in Example 1.

Example 2:

Example 2 demonstrates the growth of a S-doped InP crystal. While a non-doped single crystal that has incorporated no impurity of any sort therein is generally used as a seed crystal, it is permissible to use a crystal that has been doped with the same impurity as the crystal to be grown.

In this Example 2, a S-doped crystal grown by the VGF technique was used as a seed crystal. This seed crystal measured 51.5 mm in diameter and 20 mm in thickness and possessed an average dislocation density of 420/cm^2. The crystal, during the growth thereof, incorporated In_2S_3 as a dopant therein, with the incorporation so controlled as to adjust the carrier concentration in the growth initiating part at $1 \times 10^{18}/cm^3$. The other conditions for the growth of the crystal herein were the same as in Example 1. The crystal consequently obtained was an InP single crystal measuring 2 inches in diameter and 90 mm in total length and forming absolutely no twin crystal. When the single

crystal ingot was cut to determine dislocation density, it was found to possess an average dislocation density of 80/cm^2 and the largest dislocation density of 1000/cm^2. Not less than 95% of the 5 mm squares within the surface of the wafer possessed dislocation densities of less than 500/cm^2.

Example 3:

Example 3 demonstrated the growth of a Si-doped GaAs crystal.

The seed crystal used herein was a Si-doped GaAs crystal grown by the VGF technique. This seed crystal measured 51.5 mm in diameter and 20 mm in thickness and possessed an average dislocation density of 400/cm^2. A crucible made of PBN and measuring 52 mm in inside diameter was used and charged with 1000 g of a polycrystal raw material for GaAs and 200 g of B_2O_3. The crystal, during the growth thereof, incorporated Si as a dopant therein, with the incorporation so controlled as to adjust the carrier concentration in the growth initiating part at 7 x 10^{17}/cm^3. The crystal consequently obtained was a GaAs single crystal measuring 2 inches in diameter and 80 mm in total length and forming absolutely no twin crystal. When the single crystal ingot was cut to determine dislocation density, it was found to possess an average dislocation density of 120/cm^2 and the largest dislocation density of 1000/cm^2. As much as 96% of the 5 mm squares within the surface of the wafer possessed dislocation densities of less than 500/cm^2.

Comparative Example 1:

By following the procedure of Example 1, the growth of an InP crystal was carried out while using a non-doped InP single crystal manufactured by the ordinary LEC process and possessing an average dislocation density of 80000/cm^2 as a seed crystal instead. The non-doped crystal consequently obtained was a single crystal in which the growth initiating part possessed a dislocation density lowered to 7000/cm^2 and the trailing part of crystal revealed the presence of a polycrystal. When five experiments were carried out on the growth of an InP crystal under the same conditions, the absence of a polycrystal in the entire region from the growth initiating part through the growth terminating part was confirmed in only two of the single crystals obtained and the presence of a polycrystal in

the trailing part of crystal was confirmed in the other three single crystals.

Comparative Example 2:

By following the procedure of Example, 2 the growth of an InP crystal was carried out while using as a seed crystal a non-doped InP crystal manufactured by the VGF technique and possessing an average dislocation density of 8000/cm^2. The S-doped crystal consequently obtained was a single crystal throughout the entire region thereof and it possessed an average dislocation density of 840/cm^2 on the seed side and 520/cm^2 on the tail side. It thus failed to acquire a sufficient decrease in dislocation density as evinced by not satisfying the requirement that an S-doped InP crystal for use in a laser device be possessed of an average dislocation density of less than 500/cm^2.

Comparative Example 3:

Comparative Example 3 demonstrated the growth of a Si-doped GaAs crystal. The seed crystal used herein was a Si-doped GaAs single crystal measuring 8 mm in diameter, i.e. a greater slenderness than in Examples cited above, and possessing an average dislocation density of 400/cm^2. A crucible made of PBN and including a diameter-increased part was used herein. The appearance of this crucible and a seed crystal disposed therein is depicted in Fig. 2. The other conditions of the crucible were the same as those of Example 3. By following the procedure of Example 3, the growth of a crystal was carried out while operating the crucible as described above instead. The crystal consequently obtained was a GaAs single crystal measuring 2 inches in diameter and 80 mm in total length. When the single crystal ingot was cut to determine dislocation density, it was found to possess an average dislocation density decreased to 80/cm^2. When five experiments were carried out on the growth of a GaAs crystal under the same conditions, the absence of a twin crystal in the entire region of crystal was confirmed in only two of the single crystals obtained. In the other three single crystals, a twin crystal occurred in the entire region of crystal to the extent of lowering the yield of a single crystal.

Industrial Applicability:

The VGF technique or the VG technique according to this invention allows a single crystal of an extremely low dislocation density to be produced with a very small loss by the use of a small crucible simple in construction. Particularly, the InP single crystal and the GaAs single crystal that are obtained by the method are single crystals of low dislocation density and, therefore, are suitable as materials for electronic devices, such as high-frequency devices, high-speed electronic devices, laser devices and light-receiving devices.

CLAIMS

1. A method for the production of an InP single crystal, comprising:

gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and grow a single crystal;

causing the seed crystal to possess an average dislocation density of less than $10000/cm^2$ and assume substantially identical cross-sectional shape and size with a cross-sectional shape and size of a single crystal to be grown; and

allowing the InP single crystal to be grown to retain a non-doped state or a state doped with Fe or Sn.

2. A method according to claim 1, wherein the seed crystal is a seed crystal possessing a largest dislocation density of less than $30000/cm^2$.

3. A method according to claim 1 or claim 2, wherein the seed crystal is a seed crystal manufactured from an InP single crystal produced by the method according to claim 1 or claim 2.

4. A method for the production of an InP single crystal, comprising:

gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and consequently grow a single crystal;

causing the seed crystal to possess an average dislocation density of less than $500/cm^2$ and assume substantially identical cross-sectional shape and size with a cross-sectional shape and size of a single crystal to be grown; and

allowing the InP single crystal to be grown to retain a state doped with S or Zn.

5. A method according to claim 4, wherein the seed crystal is a seed crystal possessing a largest dislocation density of less than $3000/cm^2$.

6. A method according to claim 4 or claim 5, wherein the seed crystal is a seed crystal manufactured from an InP single crystal produced by the method according to claim 4 or claim 5.

7. A method for the production of a GaAs single crystal, comprising:

gradually cooling a molten raw material held in contact with a seed crystal to solidify the molten raw material from a lower part toward an upper part of an interior of a crucible and consequently grow a single crystal;

causing the seed crystal to possess an average dislocation density of less than $500/cm^2$ and assume substantially identical cross-sectional shape and size with a cross-sectional shape and size of a single crystal to be grown; and

allowing the GaAs single crystal to be grown to retain a state doped with Si or Zn.

8. A method according to claim 7, wherein the seed crystal is a seed crystal possessing a largest dislocation density of less than $3000/cm^2$.

9. A method according to claim 7 or claim 8, wherein the seed crystal is a seed crystal manufactured from a GaAs single crystal produced by the method according to claim 7 or claim 8.

10. A non-doped, Fe-doped or Sn-doped InP single crystal possessing a dislocation density of less than $5000/cm^2$, which is manufactured by the method according to claims 1 or claim 2.

11. A non-doped, Fe-doped or Sn-doped InP single crystal possessing a dislocation density of less than $5000/cm^2$, which is manufactured by the method according to claim 3.

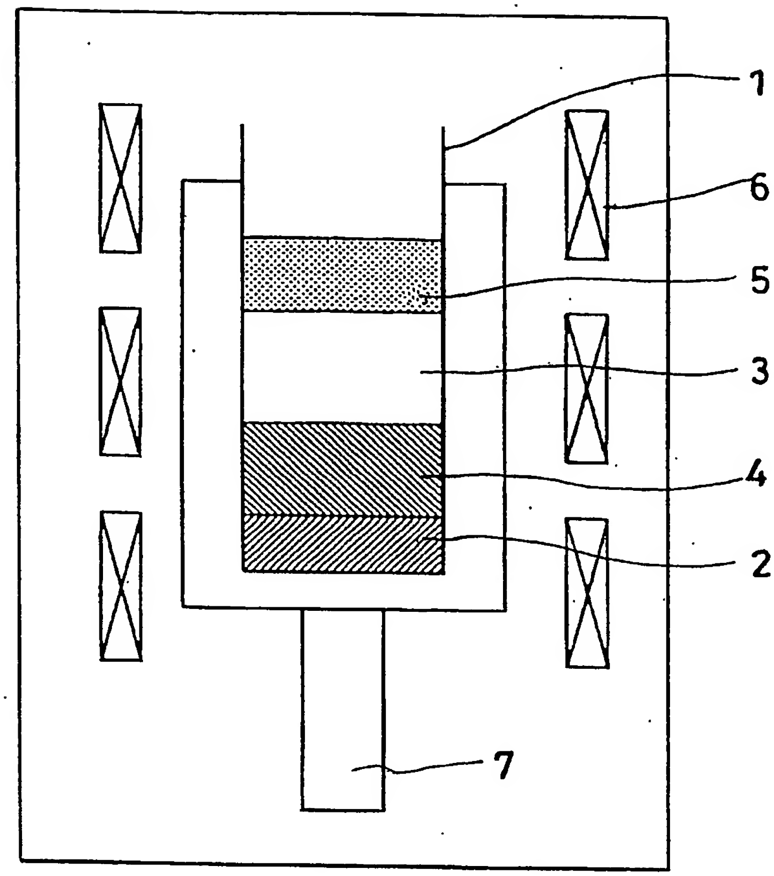
12. An S-doped or Zn-doped InP single crystal possessing a dislocation density of less than $500/cm^2$, which is manufactured by the method according to claim 4 or claim 5.

13. An S-doped or Zn-doped InP single crystal possessing a dislocation density of less than 500/cm^2, which is manufactured by the method according to claim 6.

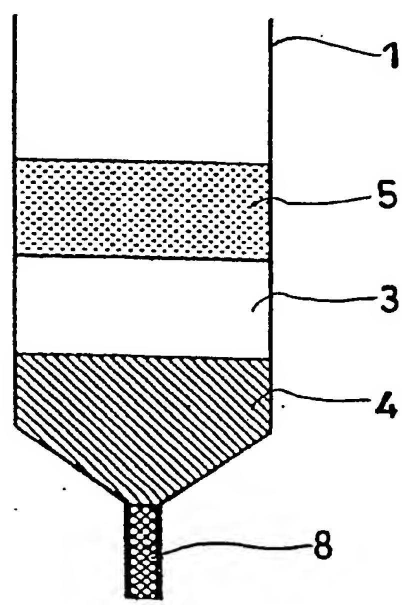
14. An Si-doped or Zn-doped GaAs single crystal possessing a dislocation density of less than 500/cm^2, which is manufactured by the method according to claim 7 or claim 8.

15. An Si-doped or Zn-doped GaAs single crystal possessing a dislocation density of less than 500/cm^2, which is manufactured by the method according to claim 9.

F I G. 1



F I G. 2



INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/010555

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C30B11/00 C30B29/40 C30B29/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GAULT: "A novel application of the verticla gradient freeze method to the growth of high quality III-V crystals" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 74, no. 3, 1986, pages 491-506, XP002121188 ISSN: 0022-0248 abstract	14,15
X	EP 0 971 052 A (MITSUBISHI CHEM CORP) 12 January 2000 (2000-01-12) claims 1,2,8,28	14,15

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 October 2004	22/10/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Cook, S

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YABUHARA Y ET AL: "High quality InP substrates grown by the VCZ method" INDIUM PHOSPHIDE AND RELATED MATERIALS, 1996. IPRM '96., EIGHTH INTERNATIONAL CONFERENCE ON SCHWABISCH-GMUND, GERMANY 21-25 APRIL 1996, NEW YORK, NY, USA,IEEE, US, 21 April 1996 (1996-04-21), pages 35-38, XP010157617 ISBN: 0-7803-3283-0 abstract	10-13
A	YASUMASA OKADA ET AL INSTITUTE OF PHYSICS: "DISLOCATION ELIMINATION IN VERTICAL GRADIENT FREEZE GROWN GAAS SINGLE CRYSTALS" GALLIUM ARSENIDE AND RELATED COMPOUNDS. JERSEY, 24 - 27 SEPT., 1990, PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON GALLIUM ARSENIDE AND RELATED COMPOUNDS. (TITLE FROM 1994 ONWARDS: PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON COMPOUND SEMICONDUCTORS, vol. SYMP. 17, 24 September 1990 (1990-09-24), pages 61-66, XP000146745 figure 1	7-9
X	ASAHI T ET AL: "VGF CRYSTAL GROWTH AND VAPOR-PHASE FE DOPING TECHNOLOGIES FOR SEMI-INSULATING 100MM DIAMETER INP SUBSTRATES" 1999 11TH. INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS. CONFERENCE PROCEEDINGS. IPRM DAVOS, MAY 16 - 20, 1999, INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS, NEW YORK, NY : IEEE, US, vol. CONF. 11, 16 May 1999 (1999-05-16), pages 249-254, XP000931439 ISBN: 0-7803-5563-6 page 252	10,11
Y	YASUMASA OKADA ET AL: "MECHANISM OF A REDUCTION OF DISLOCATION DENSITIES IN VERTICAL-GRADIENT-FREEZE-GROWN GAAS SINGLE CRYSTALS" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 29, no. 11 PART 2, 1 November 1990 (1990-11-01), pages L1954-L1956, XP000232823 ISSN: 0021-4922 page L1956, right-hand column, paragraph 2	1-15

-/--

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/010555

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 0151, no. 77 (C-0829), 7 May 1991 (1991-05-07) & JP 3 040987 A (NIPPON TELEGR & TELEPH CORP <NTT>), 21 February 1991 (1991-02-21) cited in the application abstract	7-9,14, 15
Y	ZEMKE D ET AL: "GROWTH OF INP BULK CRYSTALS BY VGF: A COMPARATIVE STUDY OF DISLOCATION DENSITY AND NUMERICAL STRESS ANALYSIS" PROCEEDINGS OF THE EIGHTH INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDEAND RELATED MATERIALS 1996. SCHWABISCH GMUND, APR. 21 - 25, 1996, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS (IPRM), NEW YORK, IEEE, US, vol. CONF. 8, 21 April 1996 (1996-04-21), pages 47-49, XP000634431 ISBN: 0-7803-3284-9 page 47, left-hand column, paragraphs 3,4	1-6, 10-13
A	EP 0 992 618 A (JAPAN ENERGY CORP) 12 April 2000 (2000-04-12) paragraphs ‘0020! - ‘0024!	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/JP2004/010555

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0971052	A	12-01-2000	DE	69914540	D1	11-03-2004
			EP	0971052	A1	12-01-2000
			JP	2000086398	A	28-03-2000
			US	6325849	B1	04-12-2001
JP 3040987	A	21-02-1991	NONE			
EP 0992618	A	12-04-2000	JP	11302094	A	02-11-1999
			JP	11343193	A	14-12-1999
			EP	0992618	A1	12-04-2000
			US	6334897	B1	01-01-2002
			WO	9950481	A1	07-10-1999

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference 6914	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/JP2004/010555	International filing date *(day/month/year)* 16 July 2004 (16.07.2004)	Priority date *(day/month/year)* 17 July 2003 (17.07.2003)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant SHOWA DENKO K.K.		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

   - [x] Box No. I — Basis of the report
   - [x] Box No. II — Priority
   - [ ] Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - [ ] Box No. IV — Lack of unity of invention
   - [x] Box No. V — Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - [ ] Box No. VI — Certain documents cited
   - [ ] Box No. VII — Certain defects in the international application
   - [ ] Box No. VIII — Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 23 January 2006 (23.01.2006)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Masashi Honda
Facsimile No. +41 22 740 14 35	Telephone No. +41 22 338 70 10

Form PCT/IB/373 (January 2004)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

RECEIVED
21 OCT 2004
WIPO PCT

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing (*day/month/year*) see form PCT/ISA/210 (second sheet)	
Applicant's or agent's file reference see form PCT/ISA/220	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date (*day/month/year*)	Priority date (*day/month/year*)
PCT/JP2004/010555	16.07.2004	17.07.2003

International Patent Classification (IPC) or both national classification and IPC
C30B11/00, C30B29/40, C30B29/42

Applicant
SHOWA DENKO K.K.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I — Basis of the opinion
- ☒ Box No. II — Priority
- ☐ Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV — Lack of unity of invention
- ☒ Box No. V — Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI — Certain documents cited
- ☐ Box No. VII — Certain defects in the international application
- ☐ Box No. VIII — Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of three months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:

European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
Fax: +31 70 340 - 3016

Authorized Officer

Cook, S

Telephone No. +31 70 340-3372

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of the international application in the language in which it was field, unless otherwise indicated under this item.

   ☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ in written format

   ☐ in computer readable form

   c. time of filing/furnishing:

   ☐ contained in the international application as filed.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. II Priority

1. ☒ The following document has not been furnished:

   ☒ copy of the earlier application whose priority has been claimed (Rule 43*bis*.1 and 66.7(a)).

   ☐ translation of the earlier application whose priority has been claimed (Rule 43*bis*.1 and 66.7(b)).

   Consequently it has not been possible to consider the validity of the priority claim. This opinion has nevertheless been established on the assumption that the relevant date is the claimed priority date.

2. ☐ This opinion has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid (Rules 43*bis*.1 and 64.1). Thus for the purposes of this opinion, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-9
	No:	Claims	10-15
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-15
Industrial applicability (IA)	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: *YABUHARA Y ET AL: "High quality InP substrates grown by the VCZ method" INDIUM PHOSPHIDE AND RELATED MATERIALS, 1996. IPRM '96., EIGHTH INTERNATIONAL CONFERENCE ON SCHWABISCH-GMUND, GERMANY 21-25 APRIL 1996, NEW YORK, NY, USA,IEEE, US, 21 April 1996 (1996-04-21), pages 35-38, XP010157617 ISBN: 0-7803-3283-0*

D2: *ASAHI T ET AL: "VGF CRYSTAL GROWTH AND VAPOR-PHASE FE DOPING TECHNOLOGIES FOR SEMI-INSULATING 100MM DIAMETER INP SUBSTRATES" 1999 11TH. INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS. CONFERENCE PROCEEDINGS. IPRM DAVOS, MAY 16 - 20, 1999, INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS, NEW YORK, NY : IEEE, US, vol. CONF. 11, 16 May 1999 (1999-05-16), pages 249-254, XP000931439 ISBN: 0-7803-5563-6*

D3: *GAULT: "A novel application of the verticla gradient freeze method to the growth of high quality III-V crystals" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 74, no. 3, 1986, pages 491-506, XP002121188 ISSN: 0022-0248*

D4: *YASUMASA OKADA ET AL: "MECHANISM OF A REDUCTION OF DISLOCATION DENSITIES IN VERTICAL-GRADIENT-FREEZE-GROWN GAAS SINGLE CRYSTALS" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 29, no. 11 PART 2, 1 November 1990 (1990-11-01), pages L1954-L1956, XP000232823 ISSN: 0021-4922*

D5: *ZEMKE D ET AL: "GROWTH OF INP BULK CRYSTALS BY VGF: A COMPARATIVE STUDY OF DISLOCATION DENSITY AND NUMERICAL STRESS ANALYSIS" PROCEEDINGS OF THE EIGHTH INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDEAND RELATED MATERIALS 1996. SCHWABISCH GMUND, APR. 21 - 25, 1996, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON INDIUM PHOSPHIDE AND RELATED MATERIALS (IPRM), NEW YORK, IEEE, US, vol. CONF. 8, 21 April 1996 (1996-04-21), pages 47-49, XP000634431 ISBN: 0-7803-3284-9*

Novelty

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 10-15 is not new in the sense of Article 33(2) PCT.

The products of claims 10-15 are taught in the prior art. D1 teaches S-doped InP single crystals with a dislocation density less than 500 cm^{-2} (see abstract).
D2 teaches undoped and Fe doped InP single crystals with average dislocation densities as low as 2000 cm^{-2} (see page 252).
D3 teaches Si-doped GaAs single crystals with dislocation densities lower than 300 cm^{-2} (see abstract).

Inventive Step

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-15 does not involve an inventive step in the sense of Article 33(3) PCT.

The problem addressed by the application is the one of producing single crystals of InP and GaAs with average dislocation densities below a given level. The solution proposed in independent claims 1,4 and 7 is to grow these crystals from the melt using a seed with a given dislocation density and a cross-sectional size and shape equal of that of the crystal to be grown. It is well known to the skilled person that the quality of a seed crystal (e.g. dislocation density) will influence the quality of the crystal to be grown therefrom. Reference is made, for example, to the very last paragraph of D4 which describes this expectation of the skilled person in relation to GaAs produced by the VGF method. The twinning problem encountered in growing crystals to a larger diameter than the seed used is also well known to the skilled person. D5, for example, describes this problem in relation to InP single crystals and informs the skilled person that the best way of overcoming the problem is to use a flat bottomed crucible with a seed the same cross-sectional size as the crystal to be grown (see fig.1 and left hand column on page 47). The independent method claims, along with their dependent claims of the present application, do not contain any technical features amounting to an inventive step when considered in the light of the skilled person's knowledge of the prior art.

Industrial applicability

The claimed subject matter is considered to be industrially applicable and thus fulfilling the requirements of Article 33(4) PCT.